

Novel Multivariate Analysis for Soil Carbon Measurements Using Laser-Induced Breakdown Spectroscopy

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Laser-induced breakdown spectroscopy (LIBS), a rapid and potentially field-deployable technology for estimating total C in soil, represents a novel approach to address important issues in soil science and C management. Our study has shown that models relating LIBS signal intensity at 247.85 nm to total C concentration determined by dry combustion vary as a function of elemental and textural characteristics of the soil, and, to a lesser extent, wavelength and excitation energy of the laser. To better quantify these sources of variation, two wavelengths and three excitation energies were used to analyze soils from various locations. The emission line of C at 247.85 nm was pronounced at an excitation wavelength of 532 nm and energy of 45 mJ, but it was largely obscured by the 248.9-nm Fe line at 1064 nm and excitation energies of 90 and 135 mJ. Univariate analysis revealed linear but soil-specific correlations between the signal intensity at 247.85 nm and total C concentration. A single and robust calibration model correlating LIBS spectra, collected at a laser wavelength of 532 nm and an excitation energy of 45 mJ, to C concentration in all samples was obtained using a multivariate approach. Several emission lines in addition to the strong C line contributed significantly to the multivariate model. These results show that multivariate analysis can be used to construct a robust calibration model for LIBS spectra and therein provide a reliable estimate of total soil C. Such results must be confirmed for a broader range of soils, yet crop and soil scientists, C managers, and instrument developers should find these results encouraging.

Abbreviations: LIBS, laser-induced breakdown spectroscopy; PC, principal component; PCA, principal component analysis; PLS, projection to latent structures; RMSEC, root mean square error of calibration.

In the last decade, soil scientists have highlighted the opportunity to manage terrestrial C stocks as a strategy to mitigate increasing CO₂ concentrations in the atmosphere (Paustian et al., 1997; Conant et al., 2001; Lal, 2004; West et al., 2008). Options for managing soil C in agroecosystems and pastures include reduced tillage and crop rotations in established croplands, improved grazing management, residue incorporation, and conservation programs. Such practices would enhance the amount of C stored in the soil and create additional land C sinks that could sequester 23 to 41 Pg C globally during the next century (Thomson et al., 2008). Quantifying changes in total soil C due to shifts in land use and land management practices has, however, proven problematic. It is clear that monitoring inventories of C stocks across agricultural landscapes will continue to be met with mixed success until more robust, rapid, and cost-effective technologies become available that are capable of measuring and verifying changes in soil C (Post et al., 2001).

To date, several promising approaches to estimate total soil C in situ have been pursued (Gehl and Rice, 2007). These range from simple yet informative correlations between soil color and soil organic C concentration (Wills et al., 2007) to more sophisticated measurements of soil C using inelastic neutron scattering and γ -ray spectroscopy (Wielopolski et al., 2000), laser-induced breakdown spectroscopy (Cremers et al., 2001; Martin et al., 2003), and near- and mid-infrared spectroscopy (McCarty et al., 2002). Each of these techniques holds promise, but each has drawbacks. The strength of inelastic neutron scattering is in its ability

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to analyze intact volumes of soil and is a truly in situ method that is capable of analyses on a large spatial scale, yet initial costs are high and operation and transport require trained radiological technicians and radiological control licenses. Near- and mid-infrared diffuse reflectance spectroscopy are less expensive and relatively simple to operate and maintain, and provide spectral data rapidly and nondestructively (Gehl and Rice, 2007; Brown et al., 2005; McCarty et al., 2002). The effect of moisture content on mid-infrared calibrations, however, is a possible concern, and carbonates complicate interpretation in both near- and mid-infrared analysis (Reeves et al., 2001). Extrapolation of existing calibration equations to soils not in calibration databases also remains a challenge in using near- and mid-infrared spectroscopy for soil C analysis.

Laser-induced breakdown spectroscopy has also emerged as a technique for measuring the elemental composition of environmental samples, including total C in soils (Cremers et al., 2001; Ebinger et al., 2003; Martin et al., 2003). The technique is appealing because it offers the soil scientist a sensitive, potentially field-portable approach to total soil C analysis that requires little sample preparation and has a potential throughput far greater than that possible with conventional dry combustion techniques (Nelson and Sommers, 1996). Despite these advantages, several uncertainties exist. Foremost among these is whether a single standardization scheme or calibration model can be devised that is robust and reproducible across a broad range of soils that differ in morphology and mineralogy. Although early attempts to relate LIBS signal intensity at 247.85 nm to C content determined by dry combustion were encouraging (Cremers et al., 2001; Martin et al., 2003), overlapping emission lines for C and Fe at approximately 248 nm led Ebinger et al. (2003) to develop a calibration model that used 193 nm instead of the more conventional 247.85-nm line. Substitution of the 193-nm emission line resulted in a highly significant linear calibration model that showed no interference with Fe for two Aridic Argiustolls and an Aridic Paleustoll in eastern Colorado. Although Ebinger et al. (2003) concluded that the calibration scheme applied to these soils was promising, they commented that additional testing would be required to evaluate the uncertainties associated with the use of LIBS to estimate total C across a more varied distribution of soil types. Soil mineralogy and morphology affect the chemical and textural characteristics of soils and introduce uncertainty into estimates of total soil C by way of matrix-mediated absorption of the emitted photons. Such effects create doubt about whether a single emission line can be used reliably to estimate soil C.

Table 1. Composition of the three different soils used in the study. Indicated values are average percentages, with the corresponding standard deviations in parentheses.

Series	Clay	Silt	Sand	Total C
	%			
Aylmer	2.6 (0.6)	2.2 (0.6)	95.2 (1.1)	0.6 (0.2)
Hoytville	53.1 (5.7)	30.8 (3.7)	16.1 (3.6)	2.8 (0.7)
Fayette	21.5 (2.8)	75.2 (2.4)	3.3 (0.8)	1.2 (0.4)

Previous research conducted at Oak Ridge and Los Alamos national laboratories has shown that several calibration models were required to quantify C concentrations when soils of different series were analyzed, and, to a lesser extent, when laser wavelength and excitation energy varied. Therefore, the first objective of this study was to evaluate how LIBS spectra collected on different types of soil varied according to laser wavelength (532 and 1064 nm) and excitation energy (45, 90, and 135 mJ). This experiment was accomplished to identify and possibly rule out operational parameters as a source of variation. The second objective was to use multivariate approaches to explore whether calibration models could be developed for LIBS that were independent of the soil chemical and physical properties. Soil samples from three distinct soil series under different land management were selected to address this objective. The overall goal was to find a set of operational parameters and statistical analysis techniques that would yield a robust calibration model or models that could be used to predict the C concentration in soils by LIBS.

MATERIALS AND METHODS

Soil samples were obtained by the NRCS from agricultural fields in Michigan, North Dakota, and Illinois as part of a national soils resource database. The soils were collected, described, treated, and analyzed using NRCS practices before subsamples were taken for this study. The Michigan samples were from the Hoytville series (fine, illitic, mesic Mollic Epiaqualfs) and were relatively high in clay content (~50%) (Table 1). The North Dakota samples were sandy from the Aylmer series (mixed, frigid Aquic Udipsamments) with up to ~95% sand. The Illinois soils were from the Fayette series (fine-silty, mixed, superactive, mesic Typic Hapludalfs) with up to ~75% silt. All of these samples were no-till soils. Furthermore, all the samples were collected from a depth of 0 to 5 cm.

Air-dried subsamples of each soil were sieved through a 2-mm mesh screen, weighed into sample containers, and analyzed for total C by dry combustion using a Vario Max CN analyzer (Elementar Americas, Hanau, Germany). Carbon concentrations averaged 0.6% for the Aylmer samples (range 0.4–0.8%), 1.2% for the Fayette samples (range 0.5–1.8%), and 2.8% for the Hoytville samples (range 1.8–4.0%). Dry soil samples were pressed into 30-mm-diameter disks using a sample press (20-ton E-Z Press, International Crystal Laboratories, Garfield, NJ) by applying ~62 MPa for ~3 min for the LIBS experiments. These pellets were very dense but craters produced by the laser could be observed under a microscope. Each sample was moved around while the data were collected. Thus, the data were not acquired from the same spot for each 100-shot average spectrum that was collected.

A total of 38 subsamples were analyzed from the three soils; nine from the Aylmer series, nine from the Fayette series, and 20 from the Hoytville series.

The LIBS experimental setup consisted of a Q-switched Nd Y Al garnet laser (Spectra Physics, Mountain View, CA) that had output wavelengths at the fundamental wavelength of 1064 nm, frequency doubled to 532 nm, and frequency quadrupled to 266 nm. The maximum beam energies at 266, 532, and 1064 nm were 80, 250, and 500 mJ per pulse, respectively. The laser pulse width was 6 to 8 ns, and the

repetition rate could be varied from 1 to 10 Hz. The laser beam had a diameter of 4 mm, and a set of lenses was used to focus the beam down to 50 μm . The focused beam generated plasma in the focal volume where all the species in the sample being examined were present. The light emitted by the plasma was collected by a second lens array situated at an angle of 45° to the direction of the laser input and was delivered to a SpectraPro-500 spectrometer (Acton Research, Acton, MA) via a C-core fiber-optic cable bundle. The resolved spectrum was detected by an intensified charge-coupled device (ICCD) built by Andor Tech (South Windsor, CT). The ICCD could be delayed and gated by a delay generator (Stanford Research Systems, Sunnyvale, CA). The smallest gate width that could be achieved by the detector was 1.2 ns. All the measurements were obtained using a 10-Hz repetition rate, and the data were averaged for 100 laser shots, which is equivalent to a 10-s spectral collection time. Since the spectrometer has mechanically mounted gratings, the collected range of the spectrum is ~ 30 nm. The center wavelength was set for a 1024-pixel window to 247.85 nm. The spectral resolution for the 30-nm window is 0.05 nm. A detailed description and drawing of the LIBS configuration can be found in Martin et al. (2003).

The extraction of the information from the LIBS spectra was achieved by using multivariate techniques such as principal component analysis (PCA) and projection to latent structures (PLS) (Martens and Næs, 1989; Næs et al., 2002) using the Unscrambler (Version 9.2) software (CAMO, Woodbridge, NJ). The package has the capability to perform both PCA and PLS. Principal component analysis is one of the most commonly utilized techniques when dealing with large and complex data sets. This projection method gives an interpretable overview of the main information in a large and complex data set by projecting the original variables (spectra) onto a smaller number of underlying variables called principal components (PCs). The first PC covers as much of the variation in the data as possible. The second PC covers as much of the remaining variation as possible, and so on. By plotting the PCs against each other, interrelations between different variables can be seen, and sample patterns, groupings, similarities, or differences can be detected.

Projection to latent structures, also known as partial least squares regression, is a relative of PCA. Projection to latent structures is the regression of a response vector (or matrix) onto a few linear combinations of the x variables (PCs) that can be used to capture significant variation in the response (y) variables. Projection to latent structures is unique in that the PLS method uses information in both the x and y variable matrices to construct PCs (referred to as *loading weights* in PLS). The advantage of this technique is that large variation in the x variables that have no impact on the response variables are ignored during modeling, and the resulting PCs will describe variation more relevant to response variable changes. The loading weight vector is calculated as the vector that maximizes the sum of the covariance between both x and y variables simultaneously. The projection of the x variables onto the loading weight vector produces scores, and the regression of the original x variables onto these scores produces regression coefficients. The regression coefficients indicate which of the original x variables are important in construction of the loading weight vector. New loading weight vectors are added until the addition of more loading weights does not decrease the residual variance of the data. Projection to latent structures uses a certain portion of the data set, called

the *calibration* data, to perform a least squares regression and estimate two important parameters in the PLS model, both loadings in terms of x and y variables. Once these parameters are estimated, they are applied to the rest of the data set for validation.

For a model to be valid, the structure of the regression coefficient and loading weight vectors should be similar, the RMSE (a measure of the precision of the model) should be relatively low, and the coefficient of correlation (r) should be sufficiently high. Projection to latent structures has proven to be useful in various calibration problems (Kelley et al., 2004; Martin et al., 2005; McCarty et al., 2002).

RESULTS AND DISCUSSION

To determine the effect of the experimental conditions on the LIBS spectra collected on various types of soils and more specifically on the C element present in the samples, LIBS data were collected by varying the laser wavelength and the excitation energy. The test conditions were 1064 and 532 nm for the wavelengths and 135, 90, and 45 mJ for the excitation energy. Figure 1 shows the spectra collected on a soil sample from Michigan under the different conditions. Analysis of the LIBS signal intensity reveals that emission lines, attributable to Si, Fe, and C, can be observed for the various combinations of laser wavelength and excitation energy. Although differences in the collected spectra are subtle, the emission lines are more pronounced for the spectra acquired at 532 nm. The intensity of the C line at 247.85 nm is noticeable at an excitation wavelength of 532 nm and energy of 90 mJ, but obscured by the 248.9-nm Fe line at 1064 nm and excitation energies of 90 and 135 mJ.

As a better way to compare and evaluate the experimental parameters' effects on the data collection, PCA was performed on the entire spectral set. Three clusters were detected based on the different wavelength and excitation energy combinations (Fig. 2). The 1064-nm, 135-mJ data set is clearly separated from

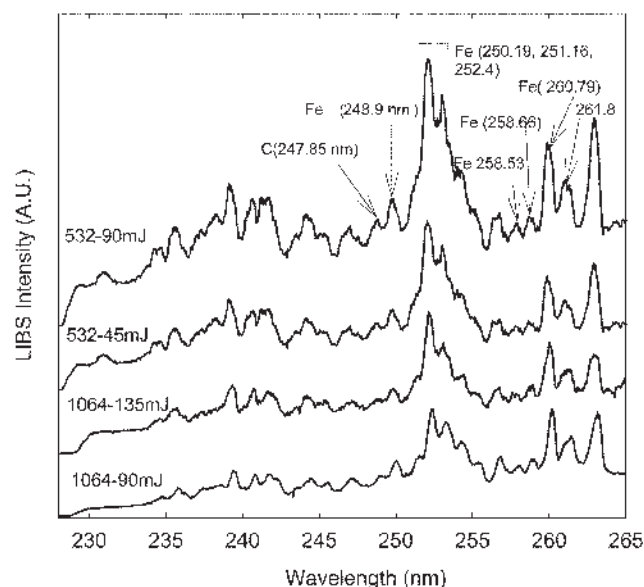


Fig. 1. Laser-induced breakdown spectra collected on a sample of the Hoytville soil under different laser-induced breakdown spectroscopy instrumental conditions.

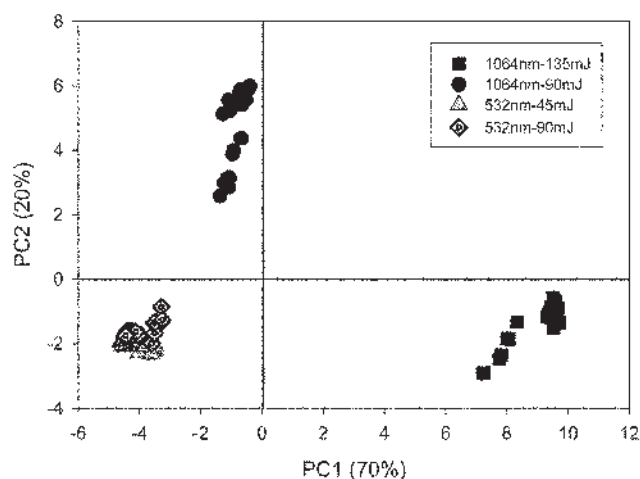


Fig. 2. Principal component analysis (PCA) score of laser-induced breakdown spectra collected on 38 soil samples with different experimental conditions.

the other sets by PC1, which accounts for 70% of the total spectral variation. The 1064-nm, 90-mJ set is separated from the two 532-nm sets by PC2, which represents 20% of the total variation. The two 532-nm tests are very close in the left negative quarter of the plot, nearly indistinct.

These results demonstrate that experimental conditions have significant effects on LIBS spectral data and suggest that there is a much greater difference among LIBS spectra when the wavelength is increased from 532 to 1064 nm. When a wavelength of 1064 nm is selected to excite a soil sample, the energy of excitation (90 or 135 mJ) also has an effect on the collected data, but less than the wavelength. These differences observed in the PCA scores plot (Fig. 2) have undoubtedly complex origins but could be partially attributed to different factors that affect the mechanism of laser-matter interactions (Francioso et al., 1998; Yang and Chase, 1998). The dependence of the spectral information on the input wavelength has been attributed to the enhancement of local fields associated with the wavelength of excitation and the predominant effect of multiphoton ionization at shorter wavelengths (Chylek et al., 1987). The energy of the 532-nm photons (2.33 eV) is greater than the energy of 1064-nm photons (1.67 eV), which means that coupling of the laser and the sample is more efficient at 532 nm than at 1064 nm. A more detailed discussion can be found in Martin and Cheng (2000). When the efficiency of coupling, and hence ionization, is high, a greater number of discernable emission lines for C and other elements can be observed (Fig. 1).

The second objective of this work was to investigate the effects of the mentioned parameters on calibration models that were developed to predict the concentration of one particular element of interest. In this study, the amount of C present in the soil samples was the property of interest. Two approaches were taken to construct the models. The first method was a univariate approach in which a model is built by correlating the intensity of a particular emission line of C to the amount present in the sample, measured by dry combustion (using a Vario Max CN analyzer). The univariate analysis was used to develop a calibration

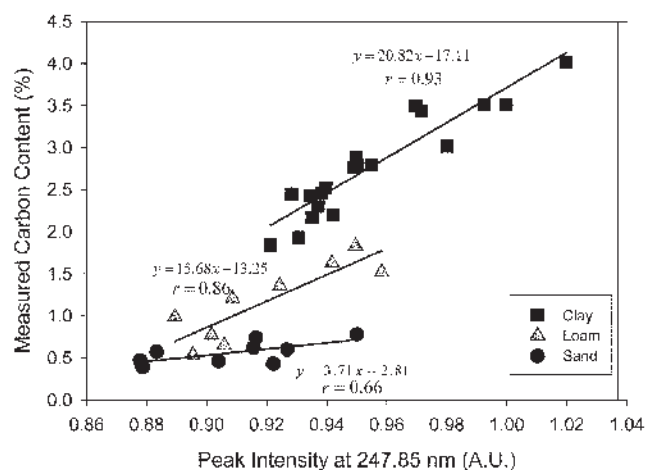


Fig. 3. Univariate laser-induced breakdown spectroscopy model for the three soil types using a 532-nm excitation wavelength with 45 mJ per pulse.

model for each soil series and for the entire 38 soil subsample data set. The models were constructed by correlating the LIBS signal intensity at 247.85 nm to the total C content. Figure 3 represents the univariate models obtained for each type of soil at 532 nm and 45 mJ as experimental conditions. The C content measured by the standard method is plotted against the intensity at 247.85 nm. As can be noted from the equations, each type of soil exhibits a different slope and intercept.

A univariate model was also constructed independently of the soil type (Fig. 4a; Table 2). A value of $r = 0.86$ was obtained from the LIBS spectra collected at 532 nm and 45 mJ. The root mean square error of calibration (RMSEC) was 0.55%. Table 2 summarizes the univariate models' results obtained for the four experimental conditions. The best univariate model, with the highest r value and the lowest RMSEC was obtained for the LIBS data collected with a laser wavelength of 532 nm and an energy of excitation of 45 mJ.

The second approach used multivariate analysis to develop PLS calibration models. Projection to latent structures constructs a regression model by correlating the entire spectrum to the property of interest. There is no need in this case to select a specific emission line for the element of interest. A summary of the various models based on the experimental conditions is presented in Table 2. Figure 4b shows the good performance of the model where predicted values of C concentration are plotted against its corresponding measured values. In such a plot, the data should fall on the diagonal (target line), i.e., predicted value = measured value when a calibration model predicts the data perfectly. To determine if the model would make a good fit for future data, a cross-validation was accomplished during the model development. During this step, each sample was left out once from the calibration data set and the model was constructed on the remaining data points. Then the value of the left-out sample was predicted with the developed model. This process was repeated until each sample has been left out once and prediction residuals were combined to calculate the root mean square error of cross validation. Figure 4b shows that the PLS model using the

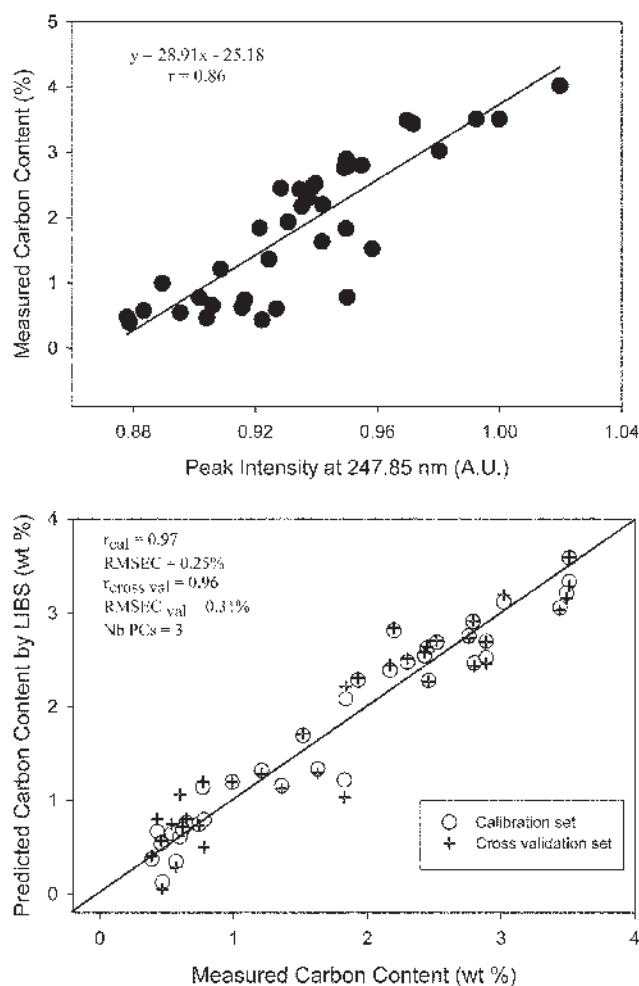


Fig. 4. Results of (a) a univariate model showing the correlation between measured C content and peak intensity at 247.85 nm collected at 532 nm and 45 mJ (for all soil samples); and (b) a multivariate model showing the correlation between measured and predicted C content with laser-induced breakdown spectra (LIBS) collected at 532 nm and 45 mJ. Solid circles and crosshairs represent the samples included in the calibration and validation sets, respectively.

data collected at 532 nm and 45 mJ yielded the best performance with almost every sample close to the diagonal.

Table 2 also provides the number of PCs that was necessary to build the best calibration models. Two to three PCs were needed to construct the PLS models. The number of samples (38) used for these calibration models is superior to the minimum number (24) required by the ASTM standard (ASTM, 2005) when three or fewer PCs are necessary to construct the models. The 38 samples are sufficient to demonstrate the feasibility and determine the optimum conditions for multivariate analysis. Independently of the experimental conditions, the highest r values were always obtained with the multivariate approach, confirming the power of the method to develop models from LIBS data to estimate total C in soils. More importantly, the models were developed for all the soil data sets. The best calibration model was obtained with the data collected at 532 nm and 45 mJ ($r_{calibration} = 0.97$ and $RMSEC = 0.25\%$) (Table 2). The regression coefficients for the PLS model for the 532-nm, 45-mJ

Table 2. Results summary for multivariate and univariate regression models built with laser-induced breakdown spectra from all soils collected under different experimental conditions.

Model	532–45 mJ	532–90 mJ	1064–90 mJ	1064–135 mJ
r_{cal} †	0.97	0.96	0.91	0.94
RMSEC, %‡	0.25	0.30	0.46	0.36
$r_{cross\ val}$ §	0.96	0.95	0.90	0.93
RMSEC _{val} , %¶	0.31	0.34	0.48	0.41
No. PCs#	3	2	2	2
$r_{univariate}$ ††	0.86	0.81	0.82	0.66
RMSEC, %‡‡	0.55	0.63	0.62	0.81

† Coefficient of correlation for calibration model.

‡ Root mean square error of calibration.

§ Coefficient of correlation for cross-validation model.

¶ Root mean square error of cross validation.

Number of principal components.

†† Coefficient of correlation for univariate model.

‡‡ Root mean square error of calibration for univariate model.

test are shown in Fig. 5a; similar plots were obtained for all other instrumental conditions (Fig. 5b, 5c, and 5d).

Several emission lines were found to be significant in constructing the PLS models from the LIBS spectra. Not surprisingly, the emission line at 247.85 nm, assigned to C, was found critical for the four models. Additionally, other wavelengths were identified as important for the models. Under the 532-nm and 45-mJ condition, emission lines at 230.30, 237.64, and 251.33 nm contributed significantly in building the calibration model (Fig. 5a). The significant line at approximately 237.6 nm was detected as well when the 1064-nm laser excitation wavelength was used (Fig. 5c and 5d). Moreover, several emission lines in the 250- to 262-nm range contributed to the models. This finding can be explained by the fact that the largest amount of inorganic C is present in the form of carbonates in the soil. These carbonates account for one-third of the total C in soil. Calcite (CaCO_3) is the most common carbonate in soil. It is known that siderite (FeCO_3), is present in soils, especially in water-logged ecosystems. Furthermore, ~50 to 70% of the dissolved organic C retained in soils contain Fe oxides and hydroxides (Jardine et al., 1989, 2006). This would explain the presence of the emission lines that were observed in our samples between 250 and 262 nm (Fig. 1) that are due to the presence of Fe in these compounds (Reader and Corliss, 1992). These peaks are 250.19 [Fe(I)], 251.16 [Fe(I)], 252.4 [Fe(I)], 258.53 [Fe(I)], 258.66 [Fe(II)], 260.79 [Fe(II)], and 261.88 nm [Fe(I)], as depicted in Fig. 1 (Reader and Corliss, 1992). The plasma that is generated by the laser excitation beam has a very high temperature of ~10,000 K, which is enough to break the bonds between the Fe, C, and O atoms present in this matrix. The Fe lines are correlated with the C peaks present in the soil samples. This explains why the lines of Fe and C co-vary.

As a result of these analyses, it is recommended that future studies use a laser wavelength of 532 nm and excitation energy of 45 mJ as experimental conditions to determine soil composition by LIBS. This study demonstrated that a multivariate model can be developed from LIBS data to predict the C content in soil.

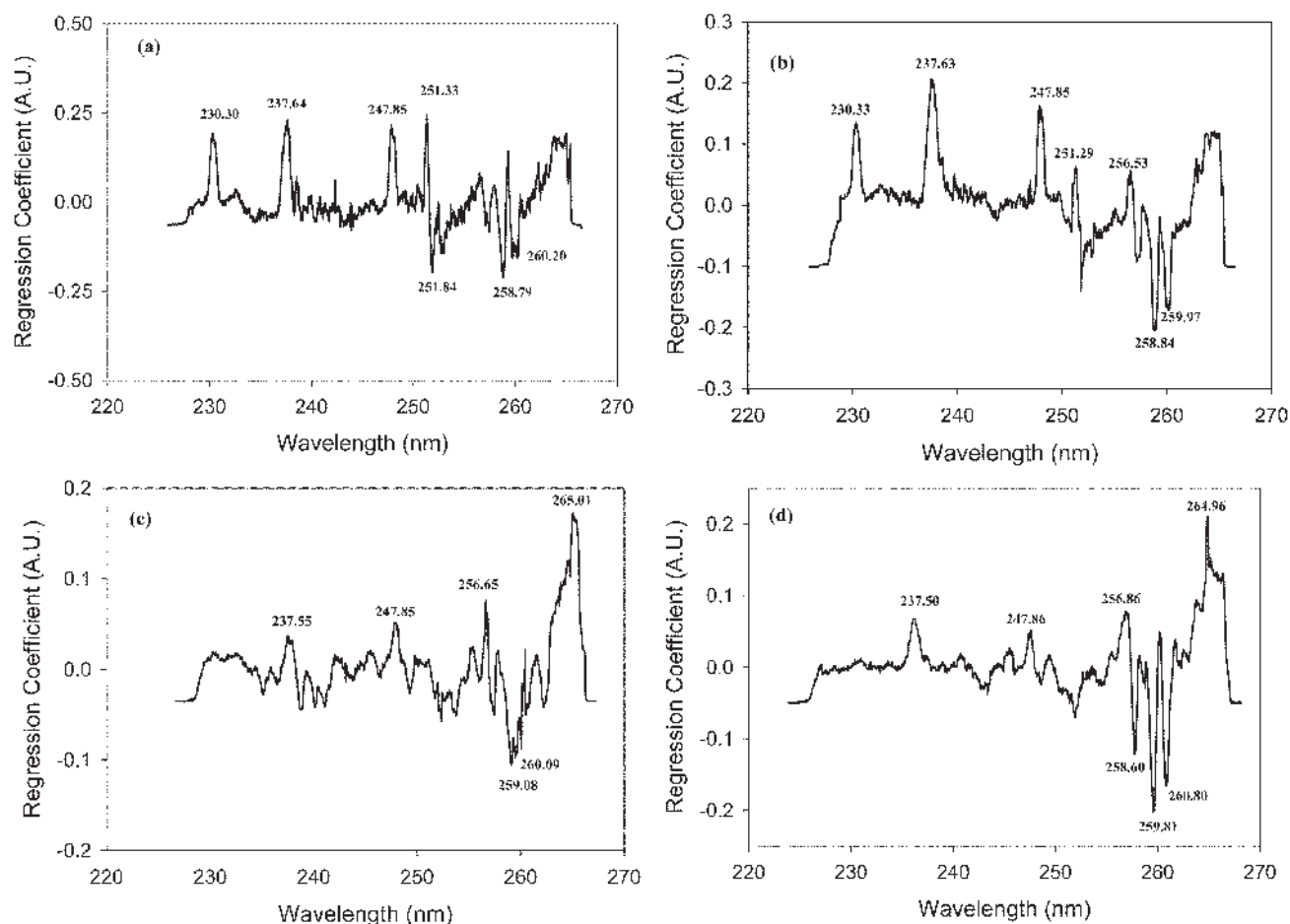


Fig. 5. Regression coefficients for projection to latent structures models predicting C content in soils from laser-induced breakdown spectroscopy data under different experimental conditions (a) 532 nm and 45 mJ, (b) 532 nm and 90 mJ, (c) 1064 nm and 90 mJ, and (d) 1064 nm and 135 mJ.

Thirty-eight samples were collected covering the C concentration range of 0.5 to 4%. Since the feasibility calibration was successful, the next step will be to expand and validate the model to make it a robust model to predict the C content in unknown soil samples.

CONCLUSIONS

There is an urgent need to develop and validate technologies capable of measuring soil C at spatial scales of interest to the soil science and C management communities. Among the options currently available, LIBS is a promising and potentially field-deployable technology, although questions exist as to sources of variation when the technique is used across a range of soils where elemental and textural characteristics of the soil and, to a lesser extent wavelength and excitation energy of the laser may influence the calibration results. From this study, the wavelength and excitation energy of the laser have been demonstrated to be important parameters when LIBS is used to determine the C concentration in soil. The highest quality data were collected with a laser that operated at a wavelength of 532 nm and an excitation energy of 45 mJ. Multivariate analysis, applied to the spectral data collected on various types of soil, has shown that LIBS can be used in the direct quantification of C in soils with different sand, silt, and clay contents. It is important to note that the soils

contain some Fe compounds and the concentration of C varies with the Fe present in the soils. A calibration model could be constructed that was independent of soil series, thus demonstrating the potential and convenience of a coupled LIBS–multivariate approach for field sampling. Obviously, these results must be confirmed for a broader range of soils and steps taken to understand the relative contributions of organic and inorganic C to the total soil C pools; however, crop and soil scientists, C managers, and instrument developers should find these results encouraging.

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